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(54) Process for the conversion of a hydrocarbonaceous feedstock

Verfahren zur Umwandlung einer Kohlenwasserstoffhaltigen Fraktion

Procédé de conversion d'une charge hydrocarbonée

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| US-A- 3 886 060 | US-A- 4 100 218 |
| US-A- 4 218 344 | US-A- 4 310 440 |
| US-A- 4 390 413 | |

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Description

The present invention relates to a process for the conversion of a hydrocarbonaceous feedstock.

In US-A-4,390,413 a process is described in which a hydrocarbonaceous feedstock is upgraded by contacting the feedstock with a ZSM-5 containing catalyst in a fixed bed reactor at a pressure below 14 bar, a temperature of 260 to 427 °C and a space velocity of 0.1 to 15 l/l.h. The feedstock must contain less than 5 ppmw of nitrogen-containing compounds, calculated as nitrogen. Although the feedstock exemplified is a gas oil, suitable feedstocks include hydrocarbons with a boiling range from 82 to 649 °C. The products include olefinic hydrocarbons, such as propene and butenes. This production of olefins is desirable, since they tend to be valuable products. The known process has the drawback that the feedstock must have been severely denitrified. This is necessary as the more nitrogenous feedstocks would deactivate the catalyst rapidly.

It has surprisingly been found that a comparatively high yield of olefins can be obtained, under less stringent conditions as regards nitrogen content, using certain zeolitic catalysts, at high temperature with a short contact time of the feedstock with the catalyst.

Accordingly, the present invention provides a process for the conversion of a hydrocarbonaceous feedstock having an end boiling point of at most 330 °C to obtain a high yield of a predominantly olefinic C₂-₄ product, which process comprises contacting the feedstock in a reaction zone, with a zeolitic catalyst comprising a zeolite with a pore diameter of 0.3 to 0.7 nm at a temperature above 500 °C during 0.2 to 0.6 seconds, and separation of product without the use of residual oil quench before the separation.

In US-A-3 886 060 a process is disclosed employing a catalyst comprising an X or Y type faujasite or a mordenite cracking component and a lower cracking activity amorphous component or an erionite, offretite or ZSM-5 small pore component for the conversion of a first stage feed comprising a recycle oil product stream of cracking and a second quench stage feed comprising a fresh residual oil whereby the effects of metal components and the coking characteristics of the residual oil feed are suppressed by means of staged injection and temperature control in individual stages.

Increase in octane value of residual oil conversion product is disclosed due to combined conversion with the recycle stream.

The surprising nature of the present invention is further illustrated by US-A-4,100,218, which describes a process for the preparation of LPG (saturated C₃-₄-hydrocarbons) and gasoline starting from an olefinic stream, using a catalyst with a pore diameter of less than 0.7 nm. Since it was known that such zeolitic catalysts have activity to catalyze the conversion of olefins to saturated and aromatic hydrocarbons, it is surprising that in the present process olefins are produced and relatively little saturated gaseous hydrocarbon product is formed.

The temperature during the reaction is above 500 °C and preferably up to 900 °C. The temperature is preferably from 550 to 800 °C.

The zeolitic catalyst comprises one or more zeolites with a pore diameter of from 0.3 to 0.7 nm. The catalyst suitably further comprises a refractory oxide that serves as binder material. Suitable refractory oxides include alumina, silica, silica-alumina, magnesia, titania, zirconia and mixtures thereof. Alumina is especially preferred. The weight ratio of refractory oxide and zeolite suitably ranges from 10:90 to 90:10, preferably from 50:50 to 85:15. The zeolitic catalyst preferably comprises as zeolite substantially only zeolites with a pore diameter of from 0.3 to 0.7 nm. Illustrative of the invention is the use of a zeolitic catalyst comprising a zeolite of pore diameter of 0.5 to 0.7 nm at a temperature above 500 °C and up to 750 °C.

The term zeolite in this specification is not to be regarded to comprise only crystalline aluminium silicates. The term also includes crystalline silica (silicalite), silicoaluminophosphates (SAPO), chromosilicates, gallium silicates, iron silicates, aluminium phosphates (ALPO), titanium aluminosilicates (TASO), boron silicates, titanium aluminophosphates (TAPO) and iron aluminosilicates. Examples of zeolites that may be used in the process of the invention and that have a pore diameter of 0.3 to 0.7 nm, include SAPO-4 and SAPO-11, which are described in US-A-4,440,871, ALPO-11, described in US-A-4,310,440, TAPO-11, described in US-A-4,500,651, TASO-45, described in EP-A-229,295, boron silicates, described in e.g. US-A-4,254,297, aluminium silicates like erionite, ferrierite, theta and the ZSM-type zeolites such as ZSM-5, ZSM-11, ZSM-12, ZSM-35, ZSM-23, and ZSM-38. Preferably the zeolite is selected from the group consisting of crystalline metal silicates having a ZSM-5 structure, ferrierite, erionite and mixtures thereof. Suitable examples of crystalline metal silicates with ZSM-5 structure are aluminium, gallium, iron, scandium, rhodium and/or chromium silicates as described in e.g. GB-B-2,110,559.

After the preparation of the zeolites usually an amount of alkali metal oxide is present in the readily prepared zeolite. Preferably the amount of alkali metal is removed by methods known in the art, such as ion exchange, optionally followed by calcination, to yield the zeolite in its hydrogen form. Preferably, the zeolite used in the present process is substantially in its hydrogen form.

The pressure in the present process can be varied within wide ranges. It is, however, preferred that the pressure is such that at the prevailing temperature the feedstock is substantially in its gaseous phase or brought thereinto by contact with the catalyst. Then it is easier to achieve the short contact times envisaged. Hence, the pressure is pref-

erably relatively low. This can be advantageous since no expensive compressors and high-pressure vessels and other equipment is necessary. A suitable pressure range is from 1 to 10 bar. Subatmospheric pressures are possible, but not preferred. It can be economically advantageous to operate at atmospheric pressure. Other gaseous materials may be present during the conversion such as steam and/or nitrogen.

5 The present process is preferably carried out in a moving bed. The bed of catalyst may move upwards or downwards. When the bed moves upwards a process somewhat similar to a fluidized catalytic cracking process is obtained.

10 During the process some coke may be formed on the catalyst. Therefore, it would be advantageous to regenerate the catalyst. Preferably the catalyst is regenerated by subjecting it after having been contacted with the feedstock to a treatment with an oxidizing gas, such as air. A continuous regeneration, similar to the regeneration carried out in a fluidized catalytic cracking process, is especially preferred.

15 If the coke formation does not occur too high a rate it would be possible to arrange for a process in which the residence time of the catalyst particles in a reaction zone is longer than the residence time of the feedstock in the reaction zone. Of course, the contact time between feedstock and catalyst should be less than 10 seconds. The contact time generally corresponds with the residence time of the feedstock. Suitably the residence time of the catalyst is from 1 to 20 times the residence time of the feedstock.

20 While the catalyst/feedstock weight ratio is not critical, it is preferred that the weight ratio varies from 1 to 150 kg or more of catalyst per kg of feedstock. Preferably, the catalyst/feedstock weight ratio is from 20 to 120:1.

25 The feedstock which is to be converted in the present process comprises hydrocarbons which have an end boiling point of at most 330°C. By this feature relatively light petroleum fractions, like naphtha and kerosine, are included. Preferably the feedstock has an initial boiling point of -45 °C. Suitable feedstocks include C₃₋₄-hydrocarbons (e.g. LPG), naphtha, gasoline fractions, kerosine fractions and mixtures thereof.

30 One of the advantages of the present invention over the process according to US-A-4,390,413 resides in the fact that a feedstock with a relatively high nitrogen content may be used with substantially no effect on the catalyst activity. Suitable feedstocks may have a nitrogen content of more than 25 ppmw, calculated as nitrogen. The feedstock may even have a nitrogen content of 100 to 1000 ppmw, calculated as nitrogen.

35 The present invention will be further illustrated by means of the following examples.

EXAMPLE 1

30 In a series of experiments a conversion process was carried out using as feedstock a C₅₋₇ hydrocarbon mixture with the following distribution:

isopentane	25.7 %wt
n-pentane	26.3 %wt
isohexane	0.3 %wt
n-hexane	23.4 %wt
isoheptane	0.8 %wt
n-heptane	23.5 %wt

40 It is observed that the boiling point of the compound with the highest boiling point is 98.5 °C.

45 The experiments were carried out in a down flow reactor in which co-currently a flow of feedstock and catalyst particles, having an average particle size of 74 micrometers, was passed downwards. The catalyst used comprised ZSM-5 in hydrogen form in an alumina matrix (weight ratio ZSM-5/alumina was 1:3). All experiments were carried out at atmospheric pressure. Further process conditions and the results of the experiments are indicated in Table 1 below.

In the table the sign "=" indicates olefinic unsaturation, and "C₅₊" indicates hydrocarbon products with 5 or more carbon atoms that are not normal or iso-paraffinic.

TABLE 1

Experiment No.	1	2	3	4
Temperature, °C	400	500	500	550
Catalyst/oil ratio, kg/kg	8.0	5.8	30.1	34.9
Contact time, s	2.0	2.0	2.0	2.0
Product, %wt				
H ₂	0.0	0.1	0.1	0.2

Continuation of the Table on the next page

TABLE 1 (continued)

Product, %wt				
C ₁	0.0	0.2	0.3	1.2
C ₂	0.2	2.4	3.3	7.5
C ₃	1.9	7.0	10.6	14.1
C ₄	2.3	4.6	7.0	7.8
i-C ₅	26.3	24.9	24.5	22.7
n-C ₅	25.8	23.9	22.7	22.1
i-C ₆	0.4	0.3	0.3	0.2
n-C ₆	20.6	18.1	14.7	12.3
i-C ₇	0.8	0.5	0.5	0.3
n-C ₇	20.0	16.3	12.9	7.2
C ₅ ⁺	0.9	0.8	1.1	1.4
coke on catalyst	0.8	0.9	2.0	3.0
Unsaturation				
C ₂ =/C ₂	1.7	1.8	1.9	1.7
C ₃ =/C ₃	0.8	1.1	1.0	1.5
C ₄ =/C ₄	0.5	1.3	1.1	1.9

From the above results it is apparent that n-paraffins are preferentially cracked and yield gaseous products which comprise a significant amount of olefins, especially at temperatures above 500 °C. Above 500 °C it will be seen that there is a markedly increased C₃ and C₄ olefin/paraffin ratio and an overall increased conversion to lower olefins. The resulting liquid product has a higher iso/normal-paraffin ratio than the starting mixture, so that, additionally, the octane number and hence the quality of the liquid product as a gasoline has been enhanced.

EXAMPLE 2

A further conversion process was carried out using as feedstock a C₅-10 hydrocarbon mixture with the following distribution (as %w on feed):

paraffins	55.9
naphthenes	32.9
aromatics	11.3
IBP	50°C
FBP	199°C
50%	119°C

The experiment was carried out at atmospheric pressure using the reactor and catalyst described in Example 1. Further process conditions and the results of the experiments are indicated in Table 2 below.

In the table the sign "=" indicates olefinic unsaturation.

TABLE 2

Process conditions:	
Reactor temperature, °C	580
Catalyst/oil ratio, g/g	112
Contact time, s	1.9
Product, %w on feed	
C ₁	1.4
C ₂	1.7
C ₂ =	7.4

Continuation of the Table on the next page

TABLE 2 (continued)

Product, %w on feed	
C ₃	4.0
C ₃ =	16.5
C ₄	2.3
C ₄ =	8.0
C ₅ -221 °C	50.5
221-370 °C	0.8
Coke	7.0

It will be noted that a high yield of a predominantly olefinic C₂₋₄ product is obtained.

15

Claims

1. A process for the conversion of a hydrocarbonaceous feedstock having an end boiling point of at most 330 °C, to obtain a high yield of a predominantly olefinic C₂₋₄ product, which process comprises contacting the feedstock in a reaction zone with a zeolitic catalyst comprising a zeolite with a pore diameter of 0.3 to 0.7 nm at a temperature above 500 °C during 0.2 to 6 seconds, and separation of product without the use of residual oil quench before the separation.
2. A process according to claim 1 in which the zeolitic catalyst comprises as zeolites only zeolites with a pore diameter of from 0.3 to 0.7 nm.
3. A process according to any of claims 1 or 2, wherein the zeolite has a pore diameter of 0.5 to 0.7 nm and the temperature is up to 750 °C.
4. A process according to any one of claims 1 to 3, in which the zeolite is selected from the group consisting of crystalline metal silicates having a ZSM-5 structure, ferrierite, erionite and mixtures thereof.
5. A process according to any one of claims 1 to 4, in which the zeolite is in its hydrogen form.
6. A process according to any one of claims 1 to 5, in which the pressure is from 1 to 10 bar.
7. A process according to any one of claims 1 to 6, in which the catalyst/feedstock weight ratio is from 1 to 150:1, preferably from 20:1 to 120:1.
8. A process according to any one of claims 1 to 7, which is carried out in a moving bed of catalyst.
9. A process according to any one of claims 1 to 8, in which the feedstock has an initial boiling point of at least -45 °C.
10. A process according to claim 9, in which the feedstock comprises C₃₋₄-hydrocarbons, naphtha, gasoline, kerosine or mixtures thereof.

Patentansprüche

1. Verfahren zur Umwandlung eines kohlenwasserstoffhaltigen Einsatzstoffs mit einem Siedeende bei höchstens 330°C zum Erhalt einer hohen Ausbeute eines hauptsächlich olefinischen C₂₋₄-Produkts, bei dem man den Einsatzstoff in einer Reaktionszone mit einem zeolithischen Katalysator mit einem Zeolith mit einem Poredurchmesser von 0,3 bis 0,7 nm bei einer Temperatur über 500°C über einen Zeitraum von 0,2 bis 6 Sekunden in Berührung bringt und das Produkt ohne vorherige Rückstandsölkühlung trennt.
2. Verfahren nach Anspruch 1, bei dem man einen zeolithischen Katalysator einsetzt, der als Zeolithe nur Zeolithe mit einem Poredurchmesser von 0,3 bis 0,7 nm enthält.

3. Verfahren nach einem der Ansprüche 1 oder 2, bei dem der Zeolith einen Porendurchmesser von 0,5 bis 0,7 nm aufweist und die Temperatur bis zu 750°C beträgt.
4. Verfahren nach einem der Ansprüche 1 bis 3, bei dem man den Zeolithen aus der Gruppe, bestehend aus kristallinen Metallsilicaten mit ZSM-5-Struktur, Ferrierit, Erionit und deren Gemischen, auswählt.
5. Verfahren nach einem der Ansprüche 1 bis 4, bei dem man den Zeolithen in seiner Wasserstoffform einsetzt.
6. Verfahren nach einem der Ansprüche 1 bis 5, bei dem der Druck 1 bis 10 bar beträgt.
- 10 7. Verfahren nach einem der Ansprüche 1 bis 6, bei dem das Gewichtsverhältnis von Katalysator zu Einsatzstoff 1 bis 150:1, vorzugsweise 20 bis 120:1 beträgt.
8. Verfahren nach einem der Ansprüche 1 bis 7, das man in einem bewegten Katalysatorbett ausführt.
- 15 9. Verfahren nach einem der Ansprüche 1 bis 8, bei dem man einen Einsatzstoff mit einem Siedeanfang bei mindestens -45°C einsetzt.
10. Verfahren nach Anspruch 9, bei dem man einen Einsatzstoff einsetzt, der C₃-C₄-Kohlenwasserstoffe, Naphtha, Benzin, Kerosin oder deren Gemische enthält.

Revendications

- 25 1. Procédé de conversion d'une charge hydrocarbonée possédant un point d'ébullition final d'au maximum 330°C en vue d'obtenir un produit à rapport paraffine en C₃ et C₄ à oléfine accru et une conversion globale en oléfines inférieures augmentée, caractérisé en ce que l'on met la charge en contact, dans une zone de réaction, avec un catalyseur zéolitique comprenant une zéolite d'un diamètre des pores de 0,3 à 0,7 nm, à une température supérieure à 500°C, pendant 0,2 à 0,6 seconde et on sépare le produit sans recourir à l'utilisation d'une suppression d'huile résiduelle avant la séparation.
- 30 2. Procédé suivant la revendication 1, caractérisé en ce que le catalyseur zéolitique ne comprend, à titre de zéolites, qu'uniquement des zéolites possédant un diamètre des pores de 0,3 à 0,7 nm.
- 35 3. Procédé suivant l'une quelconque des revendications 1 et 2, caractérisé en ce que la zéolite possède un diamètre des pores de 0,5 à 0,7 nm et la température s'élève jusqu'à 750°C.
- 40 4. Procédé suivant l'une quelconque des revendications 1 à 3, caractérisé en ce que l'on choisit la zéolite dans le groupe formé par des silicates de métaux cristallins, possédant la structure ZSM-5, la ferriérite, l'érionite et leurs mélanges.
5. Procédé suivant l'une quelconque des revendications 1 à 4, caractérisé en ce que la zéolite se présente sous sa forme hydrogène.
- 45 6. Procédé suivant l'une quelconque des revendications 1 à 5, caractérisé en ce que la pression varie de 1 à 10 bars.
7. Procédé suivant l'une quelconque des revendications 1 à 6, caractérisé en ce que le rapport pondéral catalyseur/charge fluctue de 1 à 150:1, de préférence, de 20 à 120:1.
- 50 8. Procédé suivant l'une quelconque des revendications 1 à 7, caractérisé en ce qu'on l'entreprend dans un lit de catalyseur en mouvement.
9. Procédé suivant l'une quelconque des revendications 1 à 8, caractérisé en ce que la charge possède un point d'ébullition initial d'au moins -45°C.
- 55 10. Procédé suivant la revendication 9, caractérisé en ce que la charge comprend des hydrocarbures en C₃-C₄, du naphta, de l'essence, du kérosoène ou leurs mélanges.